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# ON THE PREPARATION OF PRECURSORS AND CARRIERS OF NANOPARTICLES BY WATER JET TECHNOLOGY

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Original scientific paper
High-velocity water jet expanded into many fields of human activity due to its unique properties. Besides already traditional technological processes it begins to find its way also to the comminution of mineral particles. The paper analyzes the possibility of particle comminution using an abrasive mixing head used to generate high-velocity abrasive water jet and an impact of the jet to the solid perpendicular target made from tungsten carbide. Phyllosilicate (i.e. layered silicate) particles of both micron and submicron sizes were made by this method. The method avoids the formation of secondary structural defects which is in contrast to mechanical methods of particles comminution. Several types of micas (muscovites, vermiculite and biotite) and fine-grained kaolinites were comminuted using high-velocity water jet technology. The paper also deals with the possibilities of further change of silicate particles grain size and of using such prepared particles as precursors or carriers of nanoparticles.

**Keywords:** *carriers of nanoparticles, particle disintegration, precursors of nanoparticles, water jet*

### O pripremi supstanci i nositelja nanočestica tehnologijom vodenog mlaza

Izvorni znanstveni članak
Uporaba vodenog mlaza velike brzine proširila se u mnoga područja ljudskog djelovanja zbog njegovih jedinstvenih svojstava. Uz već tradicionalne tehnološke postupke počinje se primjenjivati u usitnjavanju mineralnih čestica. U ovom se radu analizira mogućnost usitnjavanja čestica primjenom abrazivne glave za miješanje koja stvara abrazivni vodeni mlaz velike brzine koji udara u čvrstu okomitu metu od volfram karbida. Čestice filosilikata (tj. sloja silikata) dimenzija kako mikrona tako i submikrona dobivene su ovom metodom. Ovom se metodom izbjegava stvaranje sekundarnih strukturnih defekata suprotno mehaničkim metodama usitnjavanja čestica. Nekoliko tipova mika (muskovit, vermikulit i biotit) i sitnozrnati kaoliniti usitnjeni su primjenom tehnologije vodenog mlaza. Rad se također bavi mogućnostima daljnje promjene dimenzija zrna čestica silikata te korištenja tako pripremljenih čestica kao supstance ili nositelja nanočestica.

**Ključne riječi:** *nositelji nanočestica, razbijanje čestica, supstance nanočestica, vodeni mlaz*

## 1 Introduction

Due to the unique properties of nanoparticles and possibilities of their use in daily life, nanotechnology is experiencing an unprecedented growth in recent years. However, production of industrial quantity of nanoparticles is not easy and preservation of the same properties of the final product throughout the whole technological process is still a serious problem. Nanoparticles also have a tendency to aggregate and form conglomerates due to their size. It is difficult to transport them to the location of the action or to collect and separate them for the subsequent use or safe disposal.

One solution might be to use precursors or carriers of nanoparticles. These are larger particles (of micron size) usually from a different material than nanoparticles. Nanoparticles can be cultivated on such microparticles by a definite method (e.g. action of heat, electric field or chemical processes) - such microparticle is then referred to as *precursor*, or microparticle can be used for nanoparticles transportation (nanoparticles are properly placed into microparticle structure) - then microparticle serves as a *carrier*. It is evident that the precursor can also be a carrier.

Carriers of nanoparticles may have various specific properties that are absent in particular nanoparticles (e.g. mechanical strength, abrasive resistance, sorptive properties, biocompatibility, etc.). The carriers can be used in waste water treatment and gas cleaning, or as contact sorptive-catalytic materials in insulating systems of ecological buildings, indicators of condition of concrete structures and the like. They will find application in many composite materials improving their existing capabilities or adding new features - agglomerated materials, building materials and bonding agents (corrosion resistance, increase in possible insulating effects under thermal action on steel construction of structures, increase in their stress-strain properties, aesthetic features [1] etc.), paints (increase in hardness, abrasive resistance and UV fasteness), bonding agents (plasticity and rheology), cosmetics, etc.

Nevertheless, maintaining the required quality and quantity of final product is also a problem during the preparation of microparticles. So-called micro-milling (micro-comminution) is a currently used technique to prepare micron to submicron particles of materials. Experiments performed at the Institute of Geonics demonstrated that different milling technologies produce not only various distribution of particles in the final product of disintegration, but they differ primarily in various yield of micron and sub-micron particles. Resulting product also contains particles that are disturbed intensively in a various degree even at the level of crystalline structure of the disintegrated material. Milling technology affects also morphology and specific surface of particles. Besides classic finishing procedures for the preparation of such particles (e.g. planetary mill comminution, ball mill comminution, comminution by pressure air, etc.) using of high-velocity water jet technology appears to be a suitable variant due to its properties.

## 2 Utilization of water jets in the process of particles comminution

The idea of using water jet to comminute the particles is several decades old. Already in 1986 Galecki and Mazurkiewicz [2] investigated the possibility of coal comminution which later led to a series of mill concepts for comminution of coal and ores ([3, 4, 5]). Activities in the area of coal comminution were mainly inspired by the possible use of fine coal grains in high-velocity diesel engines (e.g. [6]). The structure of coal is characterized by the presence of many cracks enhancing the comminution effect when interacting with the high velocity water flow (as shown in the following chapter). Experience with the comminution of coal resulted in the construction of a new generation of coal mill protected by the U.S. patent [7]: pressure of water during comminution process reached almost 600 MPa and productivity of the equipment approached 1000 kg/hod of the final product depending on the material comminuted. Output grain size less than 1 micron in 50 % of the product was achieved using this mill for grinding synthetic graphite particles [8]. Another laboratory mill exploiting water jets for comminution of coal allowing separation of the final product into finer and coarser fractions was presented by Bortolussi et al. [9]. They reduced the size of the original coal grains about 25 times at a water pressure of 120 MPa with their equipment. Similarly, Cui et al. [6] achieved energy savings of 50 ÷ 70 % in the preparation of very fine coal-oil suspension by water jet mill compared to traditional comminution in ball mills.

Cavitating water jet was used in laboratory experiments by Dvorský et al. [10]. Their experimental water mill was applied to comminute dispersion of silicon microparticles to nanoparticles. Cavitating jet for milling of micas was presented also by Guo and Dong [11]. They have shown in their work (among others) that the efficiency of comminution by cavitating abrasive water jet is higher than that by mechanical comminution methods.

Another concept of water mill exploiting mixing chamber and the impact of the jet on solid surface was introduced in the paper by Zonghao and Zhinan [12], who examined the wet comminution of raw salt at water pressures up to 30 MPa. They report also mechanism of salt particles disintegration using water jet. A similar method of comminution was also applied during coal disintegration by Borkowski and Borkowski [13], but at higher pressures of water (hundreds of MPa). Besides, the method of comminution of minerals using water jet with thermal shock assistance was presented in [14].

There were also other concepts of comminution by water jet such as self-resonating water mill based on opposite abrasive jets pulsating and cavitating in the built-in Helmholtz resonator [15] or simple opposite abrasive jets [16]. The latter authors, however, admit that the theoretical study of the problem of mutual interaction of two mixed jets indicates that the common mixing parameters result in a very low probability of collision of the two opposite moving particles, which was the main premise at this technique of comminution. The collisions with the water mass of the opposite jet as well as the high degree of cavitation effects obviously dominate in the interaction area.

Most methods that use comminution by mechanical parts of mill, where the water jet only helps comminution process, is strongly sensitive to the mechanical setup of all moving parts, to the exact direction of the jet at the place of action and particularly to maintaining a consistent quality of the output product throughout the comminution process [12]. In our experiments, we have tried to use as simple as possible device that exploits water jets without moving mechanical parts and without complex and demanding manufacturing of such equipment.

## 2.1 Mineral grains disintegration

Disintegration of mineral grains by high-velocity water jets is well known since emergence of abrasive water jet and the use of mineral grains as an abrasive in the process of material cutting. Destruction of abrasive grains during their interaction processes with water jet, mixing chamber walls and in focusing tube represents a negative phenomenon in the high-velocity abrasive water jet technology [17], see Fig. 1. If we look at this problem from the other side, it is possible to utilize these negative properties to preserve destructive capabilities of equipment for disintegration of mineral grains (garnets, zircon and glasses). It was found that the destruction of abrasive grains can be influenced significantly by modification of the mixing chamber design [18, 19]. Substantial part of the destruction of abrasive grains occurs due to interaction of abrasive grains with water jet and walls of the chamber. Additional destruction of grains occurs during their interaction with walls of focusing tube and with material to be cut [20].

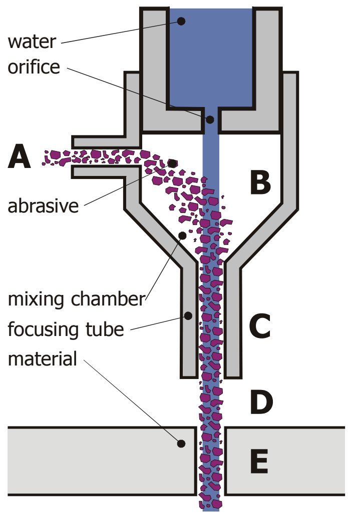



**Figure 1** Mineral abrasive particles in the process of high-velocity abrasive water jet cutting (A-input to mixing chamber, B-jet and abrasive mixing, C-focusing of the mixture, D-focusing tube output, E-material cutting)

Laboratory mill based on the principle of abrasive mixing chamber with incident target of solid material, however, is very popular among other experimenters for its efficiency, simplicity and specific properties (see e.g. [12, 13], etc.). It allows continuous comminution of materials of consistent quality and quantity of up to several kg per hour. Size of comminuted particles does not exceed 10 μm. In such a device almost any material can be milled with minimal thermal influence on the final product (no more than 70 °C). Final product is negligibly contaminated by other materials unlike some other methods of comminution (depending on the type of milled material [21]).

## 2.2 Disintegration mechanisms

Several mechanisms of disintegration of grains participating in the process of comminution of the input material to the output product can be found in various methods of material milling by high-velocity water jet or possibly with its assistance.

During interaction of the jet with milled particle so-called *fluid wedge effect* occurs (see e.g. [12, 21, 22]), as shown in Fig. 2.

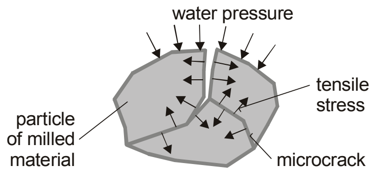



**Figure 2** Mechanism of fluid wedge effect

This effect is caused by the impact of water jet of high energy to the particle and often leads to particle breakage. Let us assume that particle enters into mixing chamber due to underpressure having initial velocity negligible to the velocity of the jet. For a given pressure $p$, the velocity of the jet impacting the particle is given by known relation based on the Bernoulli´s equation:

$$v = \mu\sqrt{\frac{2p}{\rho}}\,, \tag{1}$$

where $p$ is the pressure of water from the nozzle exit, $\rho$ is the density of the liquid medium (water) and $\mu$ is the discharge coefficient of the nozzle. At water pressures of about 400 MPa, the velocity of the jet can reach values up to 700 m/s depending on the nozzle used. Tensile stress at the walls of particle micro-cracks is generated due to the effect of compressive stress of water inside the cracks. Some particles are easily broken into smaller pieces due to exceeding of the tensile strength of the material after jet impact (tensile strength of brittle materials is much lower than their compressive strength). The particle is then accelerated in the mixing system up to the velocity of $u_p$ (see below) that can reach 0,75 of velocity of the jet $v$ [21].

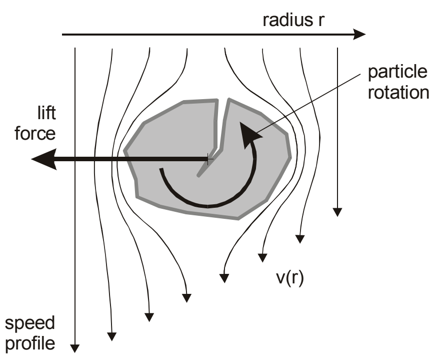



**Figure 3** Mechanism of shear disintegration in the extreme velocity gradient

Another mechanism is *shear disintegration in the extreme velocity gradient* [23]. The disintegration occurs because of rapid changes in the dynamics due to the effect of shear stresses during suspension circulation around the particles in the extreme velocity gradient of suspension flow. Thanks to the rotation and friction forces in the high-velocity gradient, the particle demonstrates also very rapid changes of intense shear stress, which leads to the destruction when the ultimate strength is exceeded (Fig. 3).

A certain amount of mainly larger particles can be broken by direct *frictional interaction with the walls of the mixing chamber and focusing tube* (see Fig. 4). Small particles under the influence of lift forces oriented to the centre of the tube usually do not come into contact with the tube wall [23]. Based on theoretical assumptions, Hlaváč and Sochor [17] similarly state that particles of milled material smaller than 5 μm are so small, that the breakage ability of water jet is not sufficient for effective disintegration of such particles in mixing chamber.

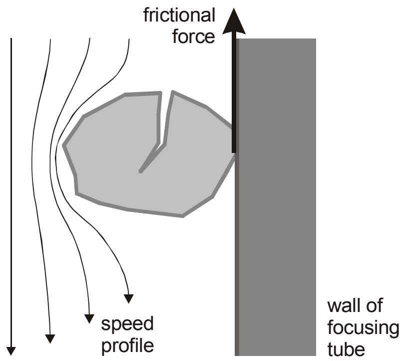



**Figure 4** Mechanism of frictional interaction with focusing tube wall

Dvorský [24] in his work describes also the mechanism of *cavitational particle disintegration*, which occurs when water jets are completely immersed into a liquid medium (Fig. 5). The collapse of cavitation bubbles on the particle surface leads to the so-called water hammer effect. Micro-jet arising from the termination of the bubble acts in the crack like a liquid wedge.

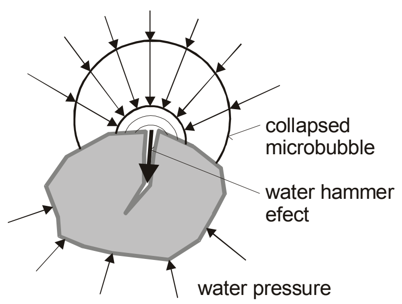



**Figure 5** Mechanism of cavitational particle disintegration

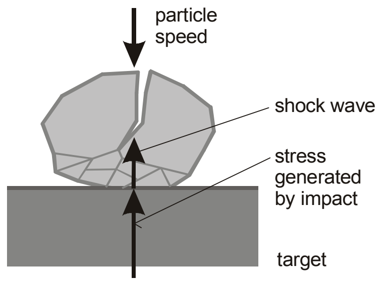



**Figure 6** Mechanical destruction of particle by its impact to target

If the abrasive jet with particles of milled material hits a solid target (see Fig. 6), mechanism of direct *mechanical destruction of particles by their impact to the target* occurs. Very fast moving water jet (1) imparts its velocity to the particle in the mixing chamber and focusing tube. Impact stress *p* generated from the impact between the particles and the target is described by Zonghao and Zhinan [12]. During the process, impact stress *p* will lead to particle crushing:

$$p = \rho_S \cdot c \cdot u_p \,, \quad (2)$$

where $\rho_S$ is the density of particle, *c* is the velocity of the wave in the grain because of impact and $u_p$ is the velocity of particles before the impact. This mechanism significantly contributes to the total disintegration and applies especially for larger particles where mass forces dominate over the hydrodynamic forces drifting particles in liquid stream [23]. Very small particles do not interact with the target, because of pulling down to the tangential direction of the streamlines of flowing around suspension (Fig. 7).

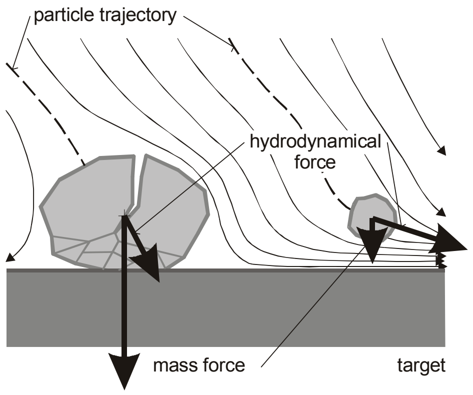



**Figure 7** Influence of particle size during impact to target

Above mentioned mechanisms do not act independently, but they are combined according to the milling method. Thereby final disintegration effect is intensified.

## 2.3 Effect of genesis of mineral grains and their crystal structure

Internal structure of the milled particles and the process of their formation and modification prior to milling (genesis) have also significant influence on the characteristics of output product in addition to the mechanisms participating in the specific technique of material comminution by water jet technology.

In the case of cubic symmetry of minerals such as garnets of pyrope (Mg) - almadine ($Fe^{+2}$) series, primary cracks of geological origin in the mineral grain (connected with grain deformation by tectonic processes) and the cracks initiated by technological processing of raw material play significant role in particle breakage. Initiation of cracks around inclusions (gaseous and solid) in the process of interaction of particles with water jet and interaction with the material cannot be omitted, too. Based on these facts one can explain the different behaviour of garnet abrasive of various genesis. For example garnet particles prepared by crushing of rocks and subsequent separation of garnet with comminution to required size behave differently than garnet concentrates obtained from natural marine and river placer deposits of heavy minerals [20]. Natural defects (micro-tension) in garnets of tectonic origin can be further eliminated e.g. by annealing of garnet at a suitable temperature finally resulting in an increase of cutting efficiency of abrasive [20, 25].

Mineral particles with different symmetry behave differently after interaction with water jet and the material. For example cleavage (001), (100), (010) is developed in olivine ($(FeMg)_2SiO_4$) with orthogonal structure. Crystallographically pre-defined cleavage of olivine abrasive grains during their failure seems to be more significant than primary inclusions and tectonically induced defects [26]. This influence is also evident on the morphology of the grains after interactive processes.

Failure of phyllosilicates such as micas (muscovite, biotite, phlogopite), chlorites, and vermiculites is very complicated. Experiments on cutting of granites and gneisses by abrasive water jet carried at the Institute of Geonics between 1992 and 1995 showed that the process of micas failure in the rocks is very specific. Follow-up experiments with comminution of micas flakes (muscovite and biotite) by water jet have shown that perfect cleavage according to base (001) occurs primarily after flake failure. At higher pressures, additional cleavage surfaces ((110) (010)) of the micas are added, significantly at biotite (it is more fragile than at muscovite). Flakes of ideal composition are very good cleavable along base (001) for vermiculite. However, industrial concentrates of vermiculite have somewhat different composition due to presence of phlogopite in flakes as an individual sequences together with sequences of vermiculite or as a mixed structure of Mg-vermiculite, Mg-phlogopite, possibly with little ingredient of Mg-chlorite. In this case, failure is controlled by preferential cleavage according to base (001) with the fact that stronger phlogopite sequences can be separated from vermiculite flake. The experimental results show that these particles are forming coarser fraction of the disintegration product. Fine particles enriched with pure vermiculite appear in the finer fractions. When comparing different methods of micas milling, one can observe also different behaviour and different destruction and deformation of flakes. The destruction of mineral particles (flakes) by water jet is specific over other methods of disintegration and leads to creation of flat, thin particles, mostly limited by plane of cleavage with maintaining of the primary structure of mineral (no amorphization of structure or disruption in the internal structure of mineral in the particles is observed) and thus also advantageous mechanical properties of flakes. This fact is applicable to technological applications of fine mica particles for example in pigments, sorption processes, and especially for technological applications in combination with nanoparticles.

Failure of semi-amorphous materials (such as glass, glassy slags and, to a certain extent, black coal to anthracites) is quite specific. For such materials, preferential planes of failure do not occur and disintegration is similar to failure of isotropic materials. The final product after disintegration of coal by water jet is strongly dependent on the maceral composition of input grains (coal is geocomposite material of various maceral composition with various portion of mineral ash). The intensity of disintegration of black coals and anthracite is more noticeable for coals above so-called critical coalification jump (e.g. [27]), where brittle vitrinite, which is easily and well breakable, occurred in the coal matrix. Therefore high productivity [7] and low energy consumption [6] often appears in the experimental works using water mills for coal comminution.

## 3 Possibilities of further change of grain size distribution and surface modification of particles

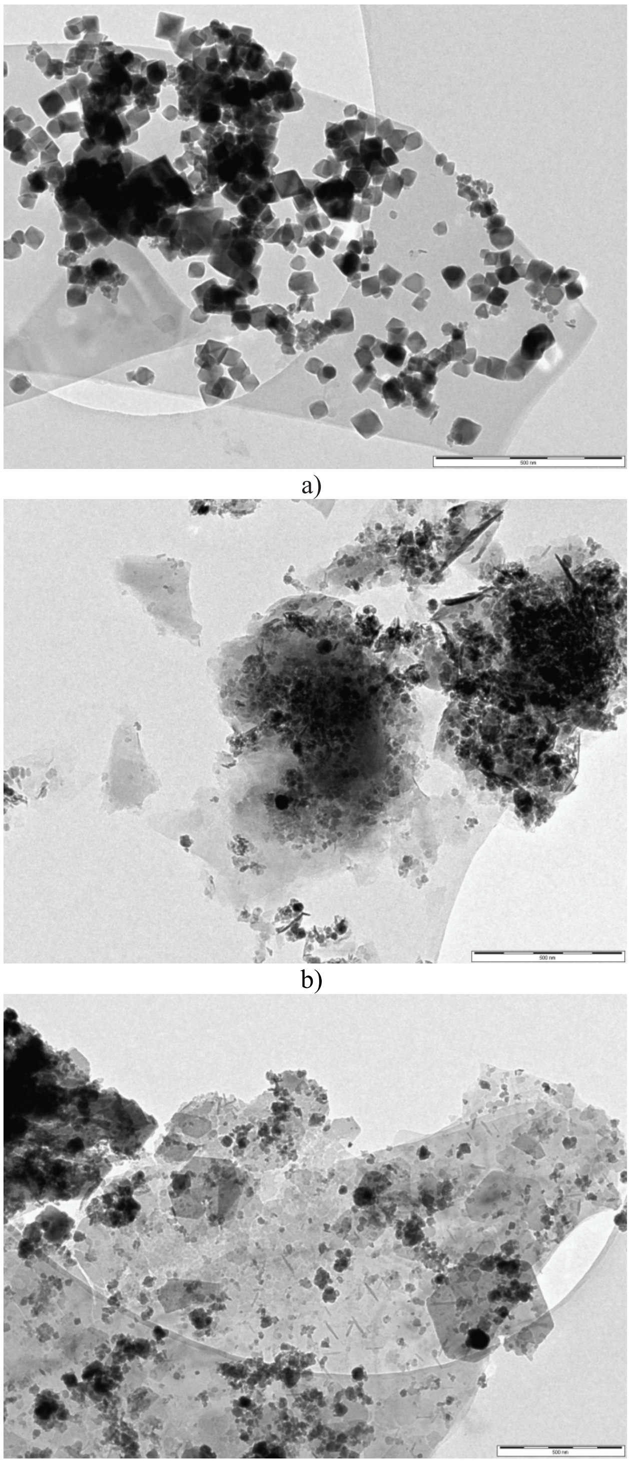
From the technological point of view, a particle with suitable size in the interval of 10 to 100 μm as well as with good mechanical properties should be created during production of precursors. These requirements are fulfilled with mica concentrates prepared by water jet comminution (see above). The product containing particles smaller than about 0,1 micron was not obtained from micas and vermiculite after water jet comminution as emerged from distribution curves. Thus, product size is in desired interval. One-peak distribution curve of product has its maximum value in the range of 20 to 40 μm (see e.g. Fig. 11). Here the question arises: Is there a possibility of further changes in particle size or changes in dispersoidal characteristics of particles by subsequent modification of the product?

In addition to mechanical methods, the product can be modified chemically. Therefore, in the second part of the experiment, chemical modification of the disintegrated product of biotite, muscovite and vermiculite was tested in order to change the distribution characteristics or to induce changes in the particle surface (etchings). This modification should also allow the separation of other (narrower) fractions of particles from disintegration product and should create conditions for better capture of nanoparticles on flakes, e.g. at defects in the structure (dislocations, failures, etched defects). Chemical methods can be used also for the preparation of nanoparticles on mineral precursors.

## 4 Preparation of nanoparticles by chemical modification of minerals

Cultivation of nanoparticles on precursors by chemical processes is described by many authors. For example Bruce et al. [28] published a method of creation of the nanoscale magnetic iron oxide particles by the alkaline oxidative hydrolysis of iron sulphate $Fe^{+2}$. An innovative idea published by Mašlán et al. [29] was chemical creation of magnetic iron oxides in the presence of fine grained minerals. The authors dealt with the attachment of magnetic nanoparticles of iron oxide on the untreated surface of muscovite, montmorillonite and vermiculite particles prepared by water jet disintegration of minerals in our laboratories.

Procedure on cultivating of nanoparticles presented in [29] is rather easy: 0,5 % suspension of 1 g of mineral (w/v) in distilled water was prepared – fine grained mineral was put on the surface of water and kept to fall down onto the bottom of the vessel, then fairly stirred to obtain homogenous suspension. The iron sulphate $Fe^{+2}$ solution (0,85 g of $FeSO_4.7H_2O$ in 10 ml of distilled water) was added to the suspension. The mixture was stirred for two hours with a magnetic stirrer. Solutions of potassium nitrate (0,5 g of $KNO_3$ in 10 ml of distilled water) and potassium hydroxide (0,7 g of KOH in 10 ml of distilled water), respectively, were added to the stirred suspension. Dark green precipitate was obtained. The stirred mixture was heated up to 90 °C and the colour of the precipitate changed to dark brown. The heating was then terminated and the suspension was stirred until it cooled to the room temperature. The composite was separated by filtration and dried on the air at the room temperature.



a) b) c)

**Figure 8** The iron oxide modified minerals: muscovite (a), montmorillonite (b) and vermiculite (c) - copied from [29]

The appearance of mineral particles with applied magnetite nanoparticles is shown in Fig 8. Based on images taken from TEM microscopy, it is evident that particles of muscovite and vermiculite prepared by water jet disintegration create thin non-deformed flakes with cleavage by base (001) with preserved original structure. Distinct deposition of magnetite nanoparticles can be observed on the particles surface. Moreover, vermiculite after water jet comminution proves noticeable failure by cleavage (see particles of hexagonal cross-section) contrary to muscovite, where the shape of the grains is not clearly affected by cleavage. Mineral particles of montmorillonite (milled and comminuted by traditional method) are very thin, irregularly deformed, with a greater portion of surface defects. Nanoparticles are accumulated mainly in agglomerates placed probably at defects or in their vicinity.

Nevertheless, nanoparticles (magnetite in our case) can be relatively easily attached on the surface of mineral particles. This fact is obvious from the mentioned images.

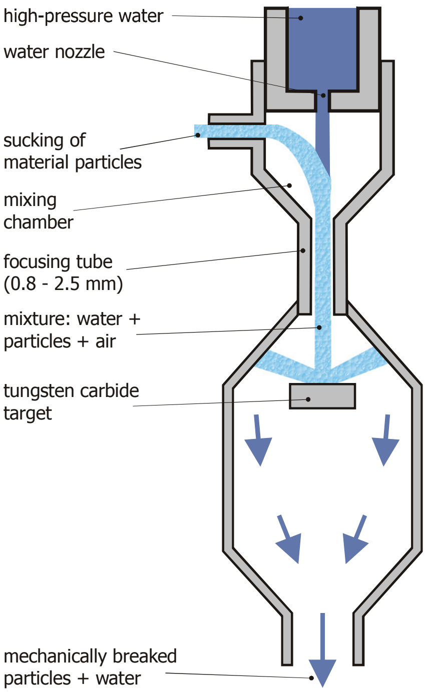



**Figure 9** Scheme of experimental water mill

## 5 Experimental equipment

Standard head PASER II (Flow) for abrasive water jet cutting with the mixing chamber and focusing tube was used for the tests of particle comminution. Milling chamber with a solid target fixed in the middle (Fig. 9) was installed below the head. Abrasive jet, where milled material of relevant grain size serves as an abrasive material, hits the solid target made from tungsten carbide. This material was chosen for its high hardness, which ensures sufficient particle breakage (see e.g. [30]). At this place, next breaking of milled material occurs due to jet impact to the target (after previous disintegration in the mixing chamber and focusing tube). Thereafter, the reflected jet hits the chamber walls, thereby the effect of disintegration increases. Some of the reflected particles can once again get into interaction with primary abrasive jet and so further disintegration of already milled material is expected. Stress intensity during the impact on the target exceeds about 40 times the tension generated during milling in a ball mill already at water pressure of 46 MPa [21], furthermore water mill thanks to its conception enables to use jets generated by water pressures up to 415 MPa, because the abrasive head is constructed for such high pressures.

High pressure pump with a multiplicator Flow delivering to the nozzle up to 3,1 litres of water per minute at a pressure of 415 MPa was used as a source of high pressure water. Particle analyzer Fritsch ANALYSETTE 22 NanoTec was used for the grain size analysis of the input and output product after water jet milling or after subsequent chemical modification. Images of milled as well as chemically activated particles were taken with a scanning electron microscope Philips XL-30.

## 6 Experimental procedure and parameters

Several types of muscovite, vermiculite and fine-grained kaolinite were comminuted using the above mentioned water mill at water pressure of 300 MPa. Some tests were done also at water pressure of 200 MPa. The diameter of water nozzle was 0,3 mm, the diameter of focusing tube was 0,8 mm and its length 76 mm. Mass flow rate of milled material depending on actual material was set in the range from 50 to 150 g/min. Milled suspension was collected in glass containers. The output product was analyzed using particle size analyzer after drying. Images of both input and output products were obtained by electron microscopy.

Chemical treatment by alkaline leaching was accomplished on the other products disintegrated by water jet (biotite, muscovite and vermiculite) after removing of coarse particles over 0,1 mm by seaving. A sample of 50 g subjected to leaching in 10 % solution of Na(OH) at 30 °C for 8 hours under continuous stirring was used in the test. During alkaline leaching, dissolving of the tetrahedron grids ($SiO_4$) and brucite (vermiculite), respectively gibbsite (biotite, muscovite) octahedron grits of layered silicate occur, in particular at places of structure disturbation or in contact of particles.

## 7 Results and discussion

Examples of results of both parts of experiment, i.e. (i) comminution of phyllosilicates by water jet technology and (ii) subsequent chemical modification of comminuted product are presented in the following sections mostly in the form of graphs.

### 7.1 Comminution by water jet

Fig. 10 and 11 represent grain size distribution of some milled materials before and after comminution at water pressures of 300 MPa and 200 MPa, respectively. Higher pressure leads to better micronization of particles, as can be seen from grain size curves of materials milled by both pressures. Higher velocity of the jet generated at higher pressure causes also higher velocity of particles and increases their energy during impact on the target. Thus, the particles are easily disintegrated to smaller sizes after impact. Similarly, fluid wedge effect is more evident at higher water pressures and jet velocities during jet impact on the particle inside mixing chamber (confirmed e.g. in [30]). Output grain size of muscovites achieved 6,7 % of input fraction, vermiculite particles were comminuted approximately to only 75 % of input fraction. It emerged that grain size of output product is strongly dependent on specific properties of comminuted material.

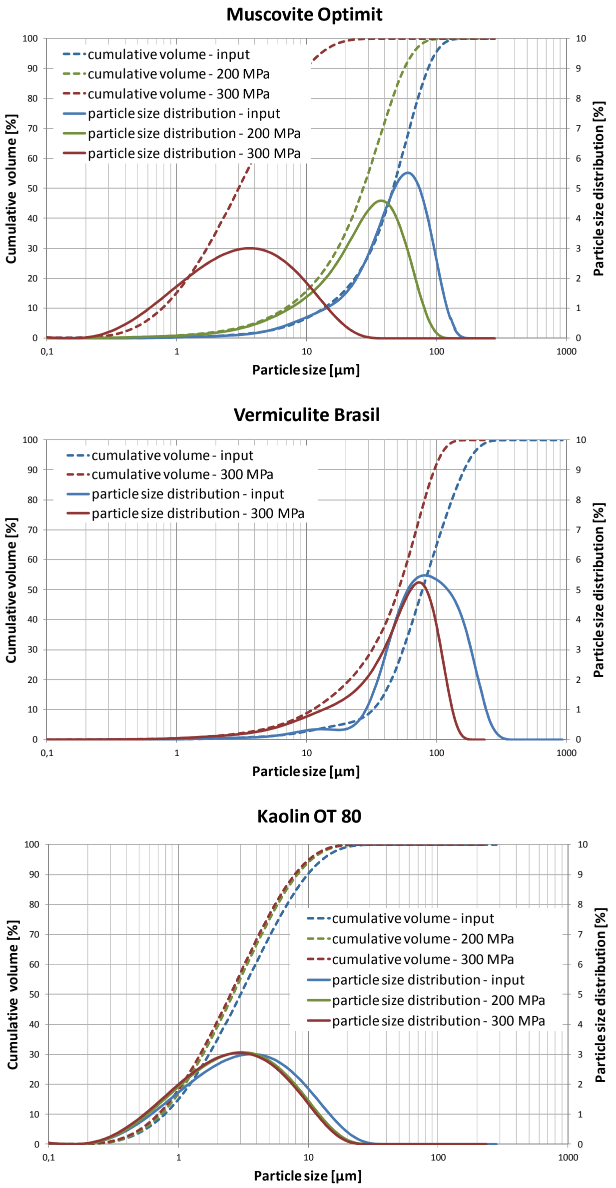



**Figure 10** Grain size curves – muscovite, vermiculite and kaolinite

Unlike micas, input kaolinites fractions were already very fine-grained (Fig. 10). Based on this fact, output fraction reached only about 80 % of the input grain size. It indicates the grain size limit which cannot be exceeded with this mill type due to the mentioned physical limitations (small particles no longer receive the required energy necessary for their impact on the target and subsequent disintegration etc. - see section 2.2). It is known from previous experiments that a finer product can be obtained by repeated milling of once milled material particles, but only to a certain threshold, given again by mill limit. This is confirmed for instance by Guo and Dong [11].

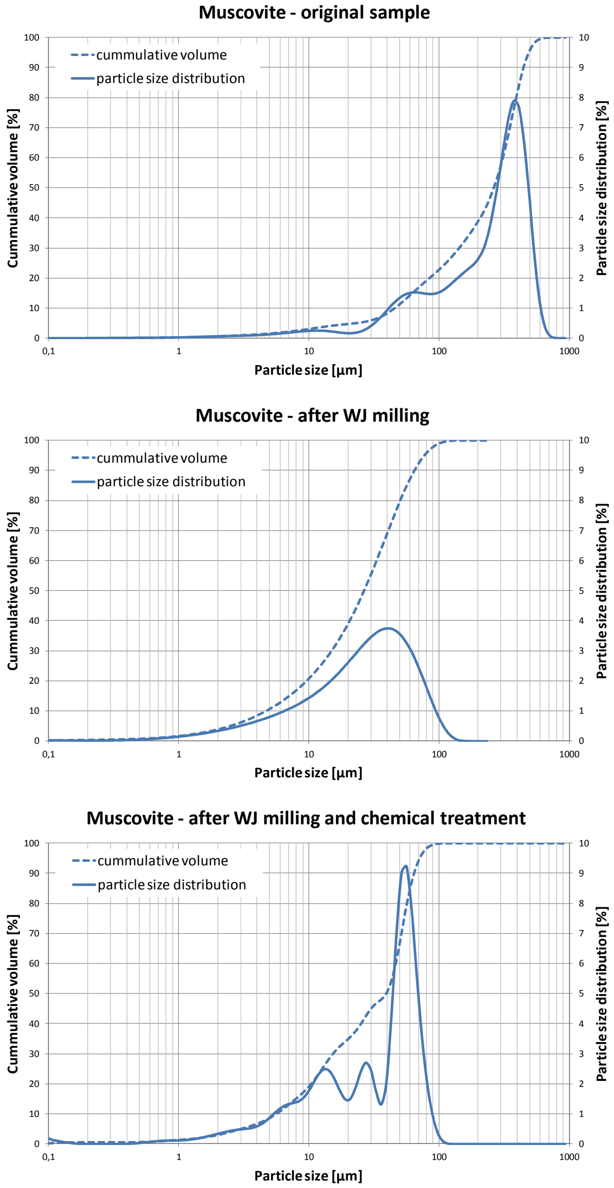
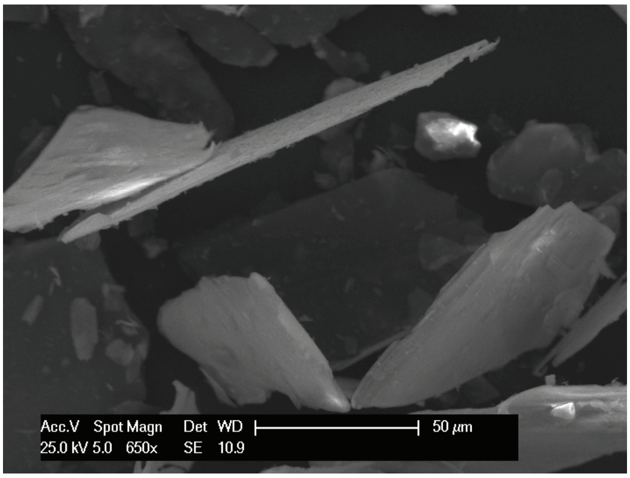



**Figure 11** Grain size curves of muscovite (Garmica) – original sample, after WJ milling, after WJ milling and chemical treatment

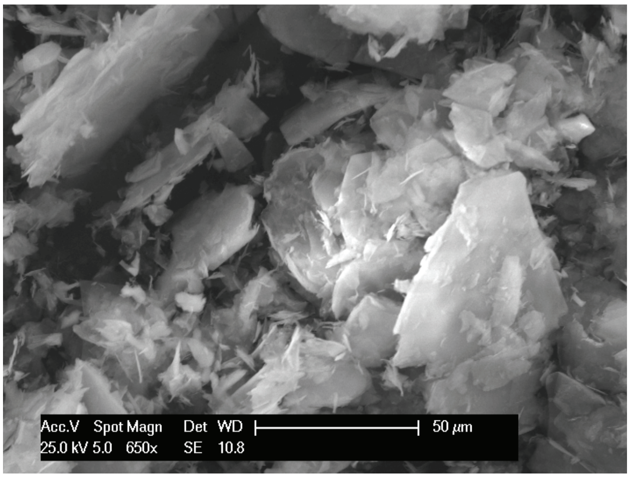
The images obtained by electron microscopy (see Fig. 12) show that the layered silicates milled by water jet preserve not only their original crystalline structure but the original physical and mechanical properties (there is no evidence of mechanical damage of particles unlike other technologies of milling, which lead to defects in the structure of minerals).

## 7.2 Subsequent chemical modification

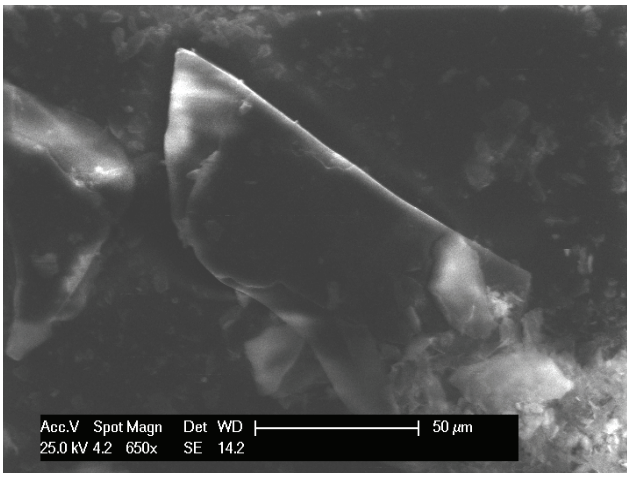
The measurements performed on chemically modified samples show that one-peak distribution curve changes to two-peaks curve (biotite, vermiculite) or three-peaks curve (muscovite) compared to disintegrated product without chemical modification. The change of dispersoidal characteristic is accompanied by the change of specific surface area to volume ratio ($cm^2/cm^3$). Dispersoidal characteristics of the original product, product after milling by water jet and product after subsequent chemical treatment are shown in Tab. 1 and Fig. 11.




A




B




C

**Figure 12** Input (A) and output product after milling by water mill (B) (muscovite Optimit Odry, water pressure 300 MPa, preserved foliaceous structure )and after following chemical treatment (C)

Particle size of the product, as well as the specific surface area after milling and after milling and chemical treatment changed very differently depending on the tested material compared to mean size and median at the input (Tab. 1). The increase in the surface between milled product and chemically modified product for vermiculite and muscovite and rather stagnation for biotite seems to be important (this is the effect of another chemical composition of mica which affects leaching).

**Table 1** Dispersoidal characteristics at input, after milling by WJ, after milling and chemical treatment. Indicated percentage part of input sample

| | Biotite / % | Muscovite / % | Vermiculite / % |
|---|---|---|---|
| | original sample | | |
| arithmetic mean | 100 | 100 | 100 |
| median | 100 | 100 | 100 |
| specific surface to volume | 100 | 100 | 100 |
| | after milling by WJ | | |
| arithmetic mean | 16,52 | 13,67 | 43,33 |
| median | 14,16 | 8,06 | 41,54 |
| specific surface to volume | 541,96 | 478,77 | 372,25 |
| | after milling by WJ and chem. treatment | | |
| arithmetic mean | 19,58 | 13,55 | 51 |
| median | 14,74 | 11,48 | 59,05 |
| specific surface to volume | 601,27 | 708,96 | 432,24 |

The presentation of dispersoidal parameters shows that each mineral has its own specifics in a transition phase of input material to the milled one (one-peak distribution curve) as well as after the chemical treatment of milled product. It is evident from the analysis that primary particles of desintegrated micas are broken-up as a result of dissolution of contact joints of particles. Distribution curve changes from one-peak curve to the curves with two peaks (vermiculite and biotite) or even three peaks (muscovite). This fact indicates the possibility of further separation of particles according to size by chemical processes.

SEM microscopy images of milled products before and after chemical treatment confirm the facts mentioned in the preceding paragraph. Untreated disintegrated particles after water jet comminution consist of thin flakes with various dimensions. Breakage of disintegrated grains occurs after chemical modification and the product is represented only by several fractions. Smaller particles seem to be removed from the final product (Fig. 12).

## 8 Conclusions

It is evident from the experiments oriented at the comminution of layered silicates in the water mill that the technology of abrasive high-velocity water jet preserves the original structure of the material and its cleavage, while other mechanical milling techniques produce defects in the structures of milled materials. Finer output product is obtained at higher water pressure, but only to a certain limit, which is unique for every comminuted material and milling water pressure. Repeated milling of already milled product allows to obtain a finer product, but again only to a specific limit. Then further milling is no longer effective in this way.

Experiments on chemical modification by alkaline leaching proved that the stuck particles or particles weakly connected are released and dispersoidal characteristic and specific surface area to the volume of grains ratio are changed due to dissolution of contact points in alkaline environment. Milled and subsequently chemically modified particles are of micron size. Their further separation according to size is possible at least to two or three grain size classes.

Due to the unique properties of disintegration technology based on water jet, the particles prepared by this method are suitable for further use as precursors and carriers of nanoparticles. The technology allows the continuous production of microparticles and their further chemical modification in industrial quantities and in consistent quality.

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